

# Inductively Coupled Plasma Mass Spectrometry Uranium Error Propagation

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## Introduction

The Hazards Control Department at Lawrence Livermore National Laboratory (LLNL) uses Inductively Coupled Plasma Mass Spectrometer (ICP/MS) technology to analyze uranium in urine. The ICP/MS used by the Hazards Control Department is a Perkin-Elmer Elan 6000 ICP/MS. The Department of Energy Laboratory Accreditation Program requires that the total error be assessed for bioassay measurements. A previous evaluation of the errors associated with the ICP/MS measurement of uranium demonstrated a  $\pm 9.6\%$  error in the range of 0.01 to 0.02  $\mu\text{g/l}$ . However, the propagation of total error for concentrations above and below this level have heretofore been undetermined. This document is an evaluation of the errors associated with the current LLNL ICP/MS method for a more expanded range of uranium concentrations.

## Method

Initial estimates of the variance for various uranium concentrations were determined using previous and concurrent QC samples. The variance was determined for ten ranges of spike levels. Based on these initial estimates of error, the number of samples necessary to establish the error within the spike range was determined using:

$$n = \frac{4\sigma^2}{L^2}$$

where:  $n$  = the number of samples

$\sigma^2$  = the estimated variance

$L$  = is the allowable error

Samples were prepared using a blank urine matrix and processed by the standard analysis method (HCL-I-3020). A 1-liter urine sample with low uranium content was acidified with nitric acid for use in this study. Aliquots were used to make blanks and NIST traceable spiked solutions. The analysis method (HCL-I-3020) uses nitric acid combined with a microwave digestion. The method also uses Uranium-233 as an internal tracer that adjusts the ICP/MS result due to degraded response during the readout process of a batch of samples. Each batch of samples contains a blank and NIST traceable uranium spikes that are used to assure the quality of the batch analysis. The current detection level is documented to be 0.002  $\mu\text{g/l}$  with a reporting level of 0.01  $\mu\text{g/l}$ . The dosimetric action level has been established as 0.05  $\mu\text{g/l}$ .

An initial evaluation of the error associated with each measurement used the difference of the measured concentration minus the known concentration. This evaluation was used to empirically determine if any of the data appeared to deviate from an expected response of decreasing error as uranium concentrations increase. The standard deviation was calculated for each set of the ten spike levels. The standard deviation was calculated for each of the ten uranium standard concentrations. The fractional error was then determined for each known concentration by dividing the standard error by the known concentration. A non-linear fit using an exponential model was then performed using the

fractional error and known uranium concentration to determine the functional relationship between these two variables.

## **Results**

Results of the analysis of blanks and known concentrations are provided in Table 1. Based on an analysis of 10 replicate blanks, the known background concentration of uranium was determined to be 0.0046 ug/l. The known uranium concentration additions were then added to the blank concentration to establish an expected concentration. This expected known concentration was established as the 'known' uranium concentration.

The percent difference between the measured and known concentration as a function of the uranium concentration can be observed in Figure 1. This difference reduced rapidly as the concentration increased from 'blank' levels to levels where the uranium can be reliably reported. After approximately 0.02 ug/l the error tends to remain fairly constant. It is noted that there is a consistent bias in the differences of approximately +5%. This bias may indicate a slight residual effect or an addition of uranium in the analysis process.

The percent error at 1 standard deviation for the ten different spike levels is illustrated in Figure 2. After 0.02 ug/l the errors tended to remain below 2%. Therefore in constructing an exponential model, a lower boundary for the error was established at 2%. Modifications of this value did not improve the fit of the data to the model. The model and visual fit of the model can also be observed in Figure 2. The correlation statistic for the non-linear fit was better than 0.99.

Table 1. Results of uranium error study

<b>Sample</b>	<b>Repl.#</b>	<b><sup>238</sup>U Concentration, µg/L</b>		
		<b>Added</b>	<b>Total Expected</b>	<b>Measured</b>
Blank	1	0	N/A	0.0044
Blank	2	0	N/A	0.0051
Blank	3	0	N/A	0.0046
Blank	4	0	N/A	0.0045
Blank	5	0	N/A	0.0058
Blank	6	0	N/A	0.0046
Blank	7	0	N/A	0.0044
Blank	8	0	N/A	0.0046
Blank	9	0	N/A	0.0040
Blank	10	0	N/A	0.0042
Blank+2	1	0.002	0.0066	0.0086
Blank+2	2	0.002	0.0066	0.0071
Blank+2	3	0.002	0.0066	0.0064
Blank+2	4	0.002	0.0066	0.0057
Blank+2	5	0.002	0.0066	0.0060
Blank+2	6	0.002	0.0066	0.0082
Blank+2	7	0.002	0.0066	0.0080
Blank+3	1	0.003	0.0076	0.0074
Blank+3	2	0.003	0.0076	0.0072
Blank+3	3	0.003	0.0076	0.0068
Blank+3	4	0.003	0.0076	0.0068
Blank+3	5	0.003	0.0076	0.0085
Blank+4	1	0.004	0.0086	0.0080
Blank+4	2	0.004	0.0086	0.0082
Blank+4	3	0.004	0.0086	0.0088
Blank+10	1	0.010	0.0146	0.0146
Blank+10	2	0.010	0.0146	0.0141
Blank+20	1	0.020	0.0246	0.0239
Blank+20	2	0.020	0.0246	0.0230
Blank+30	1	0.030	0.0346	0.0361
Blank+30	2	0.030	0.0346	0.0360
Blank+50	1	0.050	0.0546	0.0541
Blank+50	2	0.050	0.0546	0.0551
Blank+250	1	0.250	0.2546	0.2704
Blank+250	2	0.250	0.2546	0.2682
Blank+1000	1	1.000	1.005	1.0535
Blank+1000	2	1.000	1.005	1.0564
Blank+2000	1	2.000	2.005	2.1005
Blank+2000	2	2.000	2.005	2.0367

Figure 1. Difference of the measured to known uranium concentration measurement as a function of known uranium concentration.

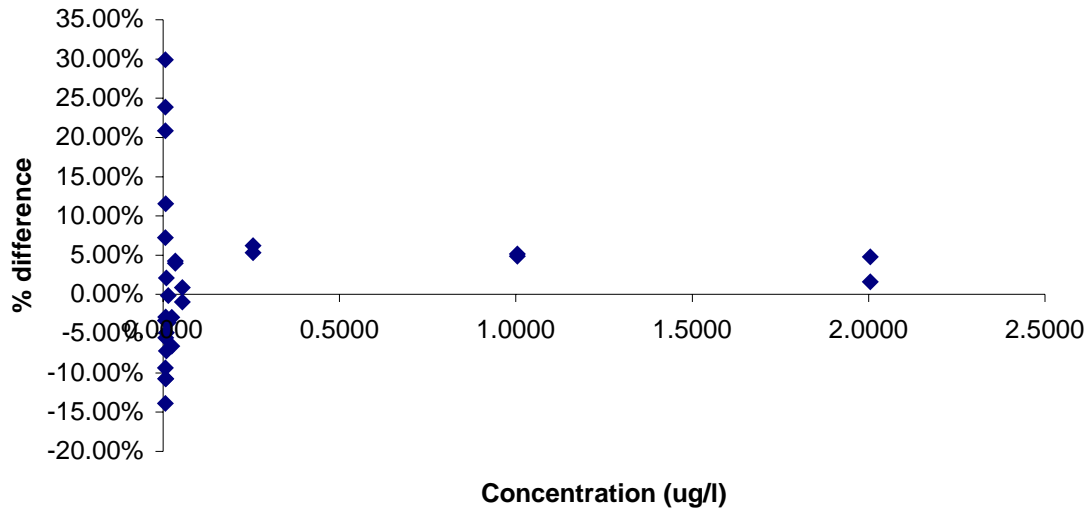
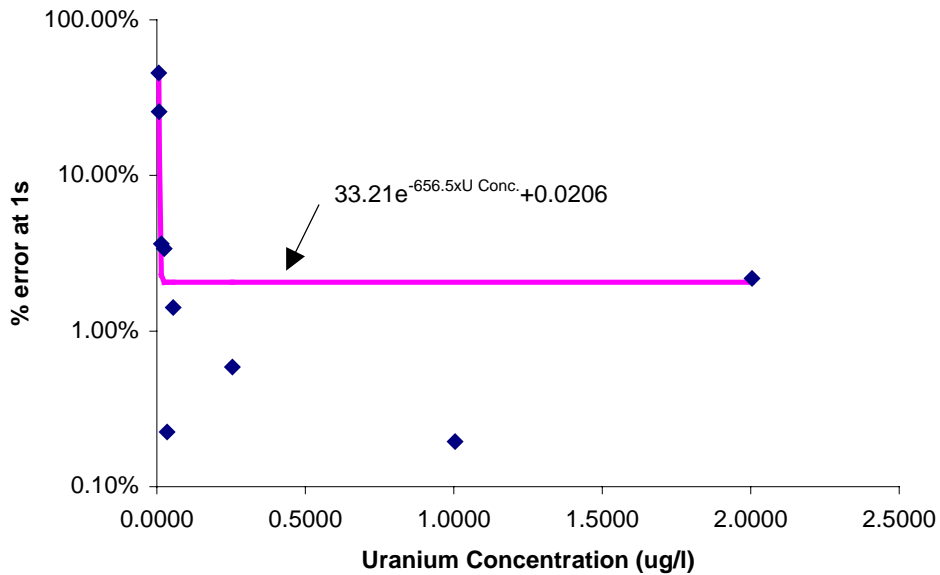


Figure 2. Percent error at one standard deviation as a function of the uranium concentration.



## Conclusions:

A previous evaluation of the errors associated with the ICP/MS analysis of uranium in urine demonstrated a  $\pm 9.6\%$  error in the range of 0.01 to 0.02  $\mu\text{g/l}$ . Using the error function derived from this study, this error at 0.01  $\mu\text{g/l}$  would be 14.5% and at 0.02  $\mu\text{g/l}$  would be 4.1%. Thus the errors observed in this study are consistent with the observed errors use in previous evaluations.

Based on the results of this experiment, the observed errors for uranium analysis with amounts ranging from 0.0076 to 2.00  $\mu\text{g/l}$  using the ICPMS is enveloped by the following function:

$$\pm 1s(\%) = 33.21 \times e^{-656.5 \times \mu\text{g} / l} + 0.0206$$

This error represents the total error associated with the analysis of urine aliquots using the ICP/MS methods developed at LLNL and should be used to propagate the total error of the analysis.

## **References**

Snedecor, G.W. and Cochran, W.G., Statistical Methods, 6<sup>th</sup> Edition, Iowa State University Press, Ames, Iowa, 1967.

SYSTAT for Windows, V6.01, “Statistics”, SPSS, 1996.